

Resolving Nanoscale Heterogeneity in Battery Interphases with Cryo-EM

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Lithium (Li)-based batteries are critical to the decarbonization of the transportation sector owing to their high energy densities [1]. However, batteries are notoriously complex, and a nanoscopic understanding of the structure and function of the various interfaces and interphases within the battery remains elusive. Most prominent among these battery structures is the solid-electrolyte interphase (SEI), a passivation layer that exists on the negative electrode (anode) of the battery [2]. This SEI has been referred to as the “most important and the least understood” aspect of the battery [3], as it dictates the stability and cyclability of the negative electrode, while remaining resistant to nanoscale interrogation by electron-optical methods such as transmission electron microscopy (TEM) as a result of their sensitivity to air, moisture, and electron irradiation. Surface-analytical techniques with poor in-plane resolution such as x-ray photoelectron spectroscopy (XPS) have thus become standard analytical techniques for the study of SEI, and anode stability is often attributed to the presence of SEI components rather than their distribution.

Owing to recent developments in cryogenic TEM for materials science, it becomes possible to image Li-based battery materials in the TEM without side reactions and beam damage, and the spatial distribution of SEI components across the anode becomes resolvable [4,5,6]. Using cryogenic scanning TEM (cryo-STEM) coupled with electron energy loss spectroscopy (EELS), we map the distribution of SEI species across the metallic Li anode, covering length scales from the nanoscale to mesoscale. We find that LiF, an SEI component believed to be indispensable to the anode performance [7], lies outside of the “compact” SEI covering the Li metal surface, which is comprised primarily of carbonates and oxides (Fig. 1). Instead, LiF precipitates across the electrode as discrete nanoparticles (Fig. 2). LiF, thought to be a critical component within the compact SEI owing to its passivating nature, likely plays a more nuanced role in the SEI. The use of high spatial resolution techniques such as Cryo-(S)TEM reveals the heterogeneous nature of SEI between the atomic and electrode length scales, which is not observable through surface analytical methods. This work bridges the gap between microscale characterizations of battery electrodes and atomic scale characterizations, revealing the nanoscale and mesoscale heterogeneity of battery interphases.

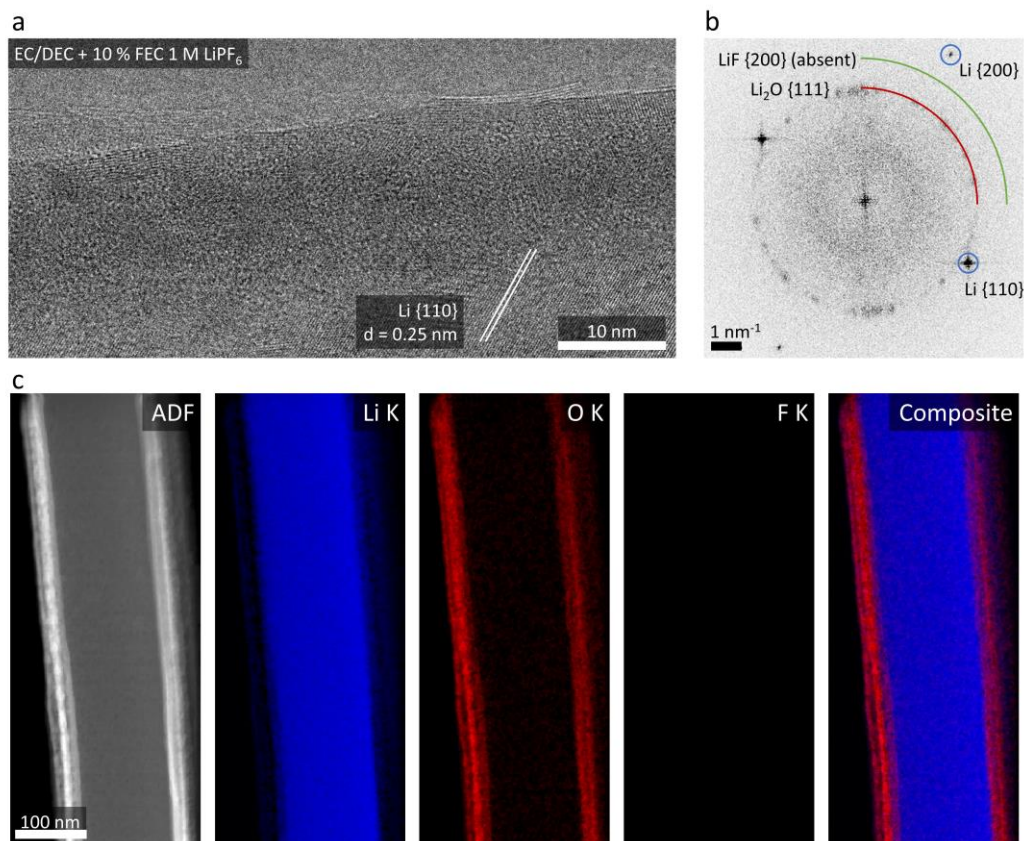


Figure 1. Cryo-(S)TEM characterization of Li metal and its compact SEI in a fluorinated electrolyte. (a) Cryo-HRTEM of the compact SEI directly interfaced with Li metal in EC/DEC 10% FEC 1.0 M LiPF₆ electrolyte. The image is 60 nm wide. (b) Fast Fourier transform (FFT) of 1d. Reflections are matched to Li₂O and Li, without any LiF reflections present. (c) Cryo-STEM EELS mapping of Li, O, F of a representative Li metal filament region without any F signal. Window is 270 nm x 640 nm.

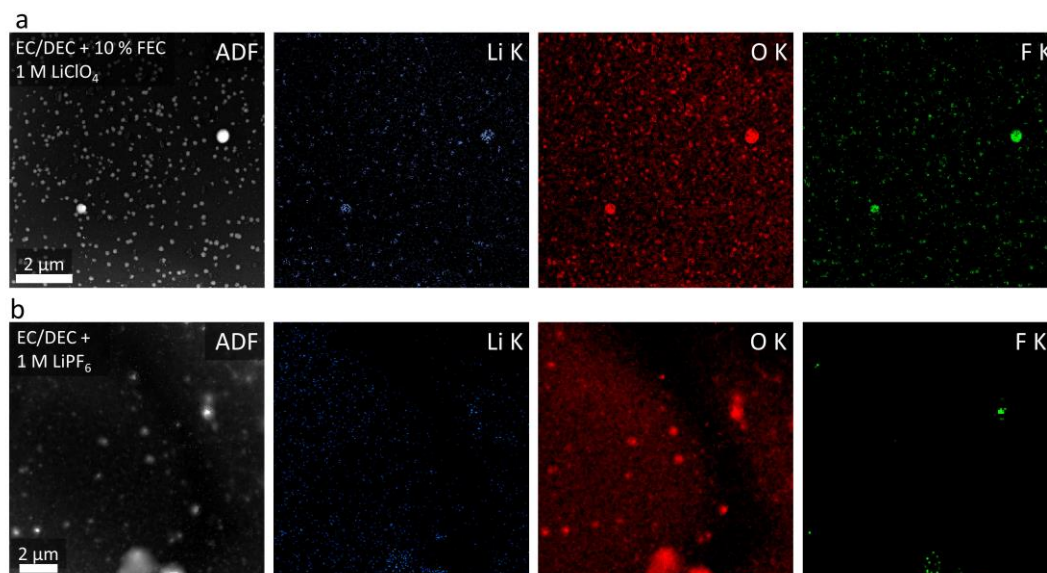


Figure 2. Cryo-STEM EELS mapping of the SEI formed on an inert, flat substrate. (a) Li, O, F mapping in a highly fluorinated electrolyte. (b) Li, O, F mapping in a standard electrolyte.

References

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